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Invariant Relationships for Heterogeneous Chemical Reaction Systems in Open Reactors

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Outline

Motivation

- Consider the following *homogeneous* reaction system - Hydrodealkylation process

$$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$$
$$2\,C_6H_6 \rightarrow C_{12}H_{10} + H_2$$

- Reaction system is operated in a batch reactor

Motivation

- The material balance equations can be written as:

$$\begin{aligned}
\dot{n}_{C_7H_8} &= -V\, r_1 & n_{C_7H_8}(0) &= n_{C_7H_8,0} \\
\dot{n}_{H_2} &= -V\, r_1 + V\, r_2 & n_{H_2}(0) &= n_{H_2,0} \\
\dot{n}_{C_6H_6} &= V\, r_1 - 2V\, r_2 & n_{C_6H_6}(0) &= n_{C_6H_6,0} \\
\dot{n}_{CH_4} &= V\, r_1 & n_{CH_4}(0) &= n_{CH_4,0} \\
\dot{n}_{C_{12}H_{10}} &= V\, r_2 & n_{C_{12}H_{10}}(0) &= n_{C_{12}H_{10},0}
\end{aligned}$$

Motivation

- In a batch reactor, we have:

$$\dot{n}_{C_7H_8(t)} + \dot{n}_{CH_4}(t) = -Vr_1 + Vr_1 = 0$$

- $n_{C_7H_8}(t) + n_{CH_4}(t)$ remains constant:

$$n_{C_7H_8}(t) + n_{CH_4}(t) = n_{C_7H_8,0} + n_{CH_4,0}$$

- Similarly, we can get other invariant relationships:

$$\begin{aligned} 2n_{H_2}(t) + n_{C_6H_6}(t) - n_{C_7H_8}(t) &= 2n_{H_2,0} + n_{C_6H_6,0} - n_{C_7H_8,0} \\ n_{C_7H_8}(t) + n_{C_{12}H_{10}}(t) - n_{H_2}(t) &= n_{C_7H_8,0} + n_{C_{12}H_{10},0} - n_{H_2,0} \end{aligned}$$

Motivation

- Invariant relationships are straightforward for an homogeneous reaction system operated in batch mode
- What are the invariant relationships for *heterogeneous* reaction systems with mass transfer between phases?
- What are the invariant relationships when the reactor has *inlet and outlet streams*?
- This contribution gives a systematic procedure for deriving the invariant relationships

Definitions

- **Reaction & Flow Variants:** Variables that vary with time due to the effects of chemical reactions and physical flows
- **Flow Variants (but Reaction Invariants):** Variables that vary with time due to other rate processes (mass transfer, inlets/outlet) but are independent of chemical reactions
- **Reaction & Flow Invariants:** Variables that do not vary with time and stay constant during the course of the reaction

Heterogeneous Reaction System: Mass Balance Equations

- Consider a multiphase reaction system
- For phase F containing S_f species, R_f reactions, p_m mass transfers, p_f inlet streams and one outlet stream, the mole balance equation can be written as:

Mole balances for S_f species

$$\dot{\mathbf{n}}_f(t) = \mathbf{N}_f^{\mathrm{T}} V_f(t)\,\mathbf{r}_f(t) + \mathbf{W}_{m,f}\,\zeta(t) + \mathbf{W}_{in,f}\,\mathbf{u}_{in,f}(t) - \frac{u_{out,f}(t)}{m_f(t)}\mathbf{n}_f(t), \quad \mathbf{n}_f(0) = \mathbf{n}_{f0}$$

$(S_f \times 1) \quad (S_f \times R_f)\ (R_f \times 1)\ (S_f \times p_m) \quad (S_f \times p_f)$

Decoupling to Vessel Extents

- Bhatt et al. introduced a linear transformation to convert the number of moles to *vessel extents*
- Recently, the transformation of Bhatt et al. has been explicited as a decoupling system inversion
- The transformation generates:
  - an extent (variant) for each of the rate processes
  - a number of invariants

N. Bhatt, M. Amrhein and D. Bonvin, Incremental Identification of Reaction and Mass - Transfer Kinetics Using the Concept of Extents, Industrial & Engineering Chemistry Research, 50(23), 12960 - 12974 (2011)

Decoupling to Vessel Extents

- Assumption:

$$\text{rank}([\mathbf{N}_f^{\mathrm{T}} \quad \mathbf{W}_{m,f} \quad \mathbf{W}_{in,f} \quad \mathbf{n}_{f0}]) = R_f + p_m + p_f + 1$$

- Linear transformation $\mathcal{T}_f$ from $\mathbf{n}_f(t)$ to extents:

$$\begin{bmatrix} \mathbf{x}_{r,f}(t) \\ \mathbf{x}_{m,f}(t) \\ \mathbf{x}_{in,f}(t) \\ x_{ic,f}(t) \\ \mathbf{x}_{iv,f}(t) \end{bmatrix} = \mathcal{T}_f \, \mathbf{n}_f(t)$$

Decoupling to Vessel Extents

- Then the system reduces to:

$$\dot{\mathbf{x}}_{r,f}(t) = \mathbf{r}_{v,f}(t) - \frac{u_{out,f}(t)}{m_f(t)}\,\mathbf{x}_{r,f}(t) \qquad \mathbf{x}_{r,f}(0) = \mathbf{0}_{R_f}$$

$$\dot{\mathbf{x}}_{m,f}(t) = \boldsymbol{\zeta}(t) - \frac{u_{out,f}(t)}{m_f(t)}\,\mathbf{x}_{m,f}(t) \qquad \mathbf{x}_{m,f}(0) = \mathbf{0}_{p_m}$$

$$\dot{\mathbf{x}}_{in,f}(t) = \mathbf{u}_{in,f}(t) - \frac{u_{out,f}(t)}{m_f(t)}\,\mathbf{x}_{in,f}(t) \qquad \mathbf{x}_{in,f}(0) = \mathbf{0}_{p_f}$$

$$\dot{x}_{ic,f}(t) = -\frac{u_{out,f}(t)}{m_f(t)}\,x_{ic,f}(t) \qquad x_{ic,f}(0) = 1$$

$$\mathbf{x}_{iv,f}(t) = \mathbf{0}_{q_f}\,.$$

- The number of invariants is: $q_f = S_f - R_f - p_m - p_f - 1$
- The number of moles can be reconstructed as:

$$\mathbf{n}_f(t) = \mathbf{N}_f^{\mathrm{T}}\,\mathbf{x}_{r,f}(t) \pm \mathbf{W}_{m,f}\,\mathbf{x}_{m,f}(t) + \mathbf{W}_{in,f}\,\mathbf{x}_{in,f}(t) + \mathbf{n}_{f0}\,x_{ic,f}(t)$$

Invariant Relationships

- The transformation matrix is computed as

$$\mathcal{T}_f = [\mathbf{N}_f^{\mathrm{T}} \ \mathbf{W}_{m,f} \ \mathbf{W}_{in,f} \ \mathbf{n}_{f0} \ \mathbf{P}_f]^{-1}$$

- where

$$\mathbf{P}_f^{\mathrm{T}} [\mathbf{N}_f^{\mathrm{T}} \ \mathbf{W}_{m,f} \ \mathbf{W}_{in,f} \ \mathbf{n}_{f0}]^{\mathrm{T}} = \mathbf{0}_{q_f \times (R_f + p_m + p_f + 1)}$$

- The invariant relationships is

$$\mathbf{P}_f^{\mathrm{T}} \mathbf{n}_f(t) = \mathbf{0}_{q_f}$$

Invariant Relationships - Flow rate Measurements

- If flowrate measurements are available, then

$$\dot{\mathbf{x}}_{in,f}(t) = \mathbf{u}_{in,f}(t) - \frac{u_{out,f}(t)}{m_f(t)}\,\mathbf{x}_{in,f}(t) \qquad \mathbf{x}_{in,f}(0) = \mathbf{0}_{p_f}$$

$$\dot{x}_{ic,f}(t) = -\frac{u_{out,f}(t)}{m_f(t)}\,x_{ic,f}(t) \qquad x_{ic,f}(0) = 1$$

- Compute the vector of reduced numbers of moles:

$$\begin{aligned}\mathbf{n}_f^{vRMV}(t) &= \mathbf{n}_f(t) - \mathbf{W}_{in,f}\,\mathbf{x}_{in,f}(t) - \mathbf{n}_{f0}\,x_{ic,f}(t)\\ &= \mathbf{N}_f^{\mathrm{T}}\,\mathbf{x}_{r,f}(t) + \mathbf{W}_{m,f}\,\mathbf{x}_{m,f}(t).\end{aligned}$$

- Assumption: rank $([\mathbf{N}_f^{\mathrm{T}}\ \ \mathbf{W}_{m,f}]) = R_f + p_m$

$$\begin{bmatrix}\mathbf{x}_{r,f}(t)\\ \mathbf{x}_{m,f}(t)\\ \mathbf{x}_{iv,f}(t)\end{bmatrix} = \mathcal{T}_f^{vRMV}\,\mathbf{n}_f^{vRMV}(t)$$

Invariant Relationships

- The transformation matrix is given by

$$\mathcal{T}_f = [\mathbf{N}_f^{\mathrm{T}} \;\; \mathbf{W}_{m,f} \;\; \mathbf{P}_f^{vRMV}]^{-1}$$

- where

$$(\mathbf{P}_f^{vRMV})^{\mathrm{T}} [\mathbf{N}_f^{\mathrm{T}} \;\; \mathbf{W}_{m,f}] = \mathbf{0}_{q_f \times (R_f + p_m)}$$

- The invariant relationships is

$$(\mathbf{P}_f^{vRMV})^{\mathrm{T}} \, \mathbf{n}_f^{vRMV}(t) = \mathbf{0}_{q_f}$$

- Note that the number of invariants is : $q_f = S_f - R_f - p_m$

Application - Data Reconciliation

- The invariant relationships can be used directly to improve the accuracy of the measurements
- Additional positivity constraints can also be imposed

$$\begin{aligned} \underset{\hat{\mathbf{n}}_f(t)}{\text{minimize}} \quad & (\tilde{\mathbf{n}}_f(t) - \hat{\mathbf{n}}_f(t))^{\mathrm{T}} \ \Sigma_n^{-1} \ (\tilde{\mathbf{n}}_f(t) - \hat{\mathbf{n}}_f(t)) \\ \text{subject to} \quad & \mathbf{P}_f^{\mathrm{T}} \, \hat{\mathbf{n}}_f(t) = \mathbf{0}_q \\ & \hat{\mathbf{n}}_f(t) \geq \mathbf{0}_S \end{aligned}$$

Example - Data Reconciliation

- Consider the following gas-liquid reaction system

$$BA_{(l)} + Cl_{2(g)} \rightarrow MBA_{(l)} + HCl_{(l)}$$
$$BA_{(l)} + 2Cl_{2(g)} \rightarrow DBA_{(l)} + 2HCl_{(l)}$$

- Chlorine is fed in the gas phase and transfers to the liquid
- The liquid phase has an outlet stream with a measured flowrate
- BA is present initially in the liquid phase

Example - Data Reconciliation

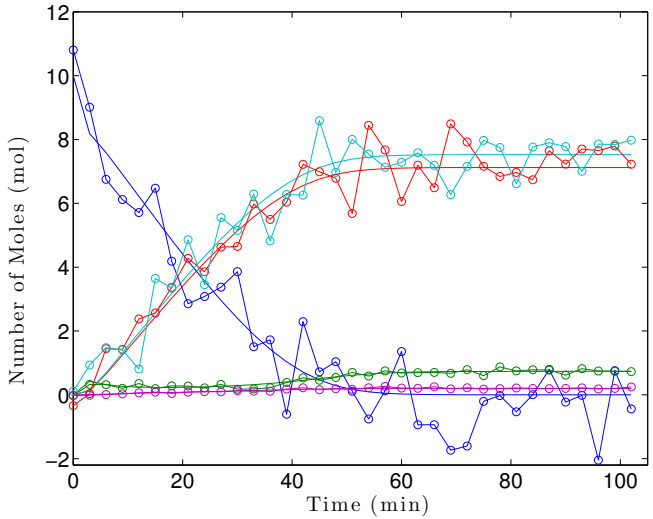
- Compute $\mathbf{n}^{vRMV}$
- Compute: $(\mathbf{P}_I^{vRMV})^{\mathrm{T}} [\mathbf{N}_I^{\mathrm{T}} \ \mathbf{W}_{m,I}]^{\mathrm{T}} = \mathbf{0}_{2\times 3}$

$$\mathbf{N}_I = \begin{bmatrix} -1 & -1 & 1 & 1 & 0 \\ -1 & -2 & 0 & 1 & 2 \end{bmatrix} \quad \mathbf{W}_{m,I} = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \end{bmatrix}$$

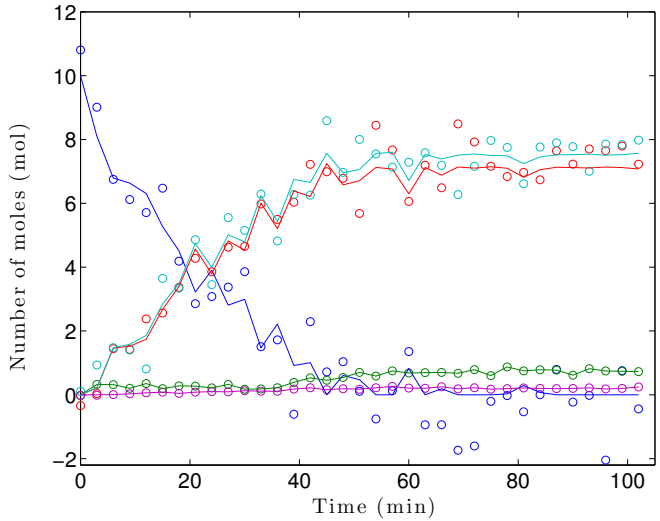
$$(\mathbf{P}_I^{vRMV})^{\mathrm{T}} = \begin{bmatrix} 2 & 0 & 1 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 \end{bmatrix}$$

Example - Data Reconciliation

- The measured numbers of moles are corrupted with 10% gaussian white noise



(a) Measured Concentrations



(b) Reconciled Concentrations

Example - Data Reconciliation

- Sum of squares between the simulated (true) and the measured/reconciled numbers of moles in the liquid phase

Species	Residual sum of squares		
	Measure-ments	With Rec-onciliation	With Rec-onciliation + positivity
BA	30.5	6.7270	4.4418
Cl_2	0.1804	0.1804	0.1799
MBA	12.5	6.7910	4.5385
DBA	15.6	6.7008	4.3820
HCl	0.019	0.0189	0.0184

Conclusion

- Systematic procedure for deriving the invariant relationships for *heterogeneous* chemical reaction systems in *open reactors*
- Successful application to data reconciliation
- Thank you for your attention

References

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